

INELASTIC NEUTRON SCATTERING FROM FILLED ELASTOMERS

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ABSTRACT

Inelastic neutron scattering experiments are powerful techniques for evaluating local molecular dynamics. These methods are especially sensitive to hydrogen atoms containing motions. An overview of these experimental techniques is presented. Neutron filter analyzer and time-of-flight spectroscopy methods are used to characterize the local dynamics of polymers in the presence and absence of fillers. Of particular interest is the comparison between bound rubber attached to the filler surface and the pure, unbound rubber. A commercial synthetic polyisoprene containing approximately 100% cis-1,4 isomers was compounded with three different carbon blacks: N299, G299 (graphitized N299), and N762. Soxhlet extraction on each of the samples was performed so that corresponding samples containing purely bound rubber with filler were obtained. The filter analyzer and time-of-flight spectra show distinct differences between the bound and pure rubber as well as differences based on carbon black type. Correlation of the spectral differences to the type of carbon black and initial concentration of carbon black are discussed.

INTRODUCTION

The reinforcement of polymers by adding inexpensive, powdered, extending agents (fillers) is a practice which dates back to the introduction of polymers as commodity materials. By adding fillers to polymers, significant reductions in production costs were achieved. One of the most commonly used fillers, predominately by the rubber industry, is carbon black. The discovery of the reinforcing nature of carbon black in rubbers is considered to be the single most important finding for the tire and rubber industry. A tremendous body of literature exists and an enormous amount of research effort has been expended to examine the nature of carbon black reinforcement in rubbers.¹ In spite of this effort, a satisfactory understanding of the mechanism of reinforcement in filled polymers is lacking.

One of the primary areas of focus for understanding the mechanism of filler reinforcement is the concept of "bound" rubber. When carbon black is compounded with a polymer, a certain fraction of the unvulcanized polymer, known as the "bound" rubber fraction, irreversibly adsorbs to the carbon black surface. The amount of bound rubber is known to change with a number of different variables. Some of these variables include the type, surface activity, surface area, concentration, and particle size of the carbon black as well as the chemical structure, molecular mass,² and microstructure of the polymer. It is presumed that the bound rubber content is a reflection of the polymer-surface interaction or the filler surface activity. The bound rubber is assumed to form a shell of less mobile polymer material around the filler aggregates. The presence of the bound rubber is related to the amount of agglomeration of the carbon black aggregates. The thickness and volume of this shell

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are the subject of much debate. It is assumed the shell is not a discrete entity, therefore, the nature of the boundary between the bound and unbound fractions is also of interest.

While the presence of bound rubber is assumed to play a pivotal role in the reinforcement of rubbers by carbon blacks, a number of questions remain. Among these questions are the following: For any given polymer chain which is bound to the filler, what fraction of the monomer units are interacting with the surface? Are the polymer-surface interactions uniform? What is the extent of the immobilization of the polymers in the bound fraction? Can this immobilization be quantified? What is the dependence of this immobilization on other variables, such as those mentioned above? Is there an analytical relationship between the amount of bound rubber, the extent of immobilization and the resultant reinforcement that is obtained in carbon black-filled polymers?

In an attempt to answer some of these questions, we have undertaken inelastic neutron scattering measurements on carbon black-filled polymers. We have measured the inelastic neutron scattering spectra of pure polyisoprene and polyisoprene compounded with three different grades of carbon black—N299, G299 (graphitized N299), and N762—after Soxhlet extraction in toluene for 72 h. The spectra are therefore representative of the unbound rubber and bound rubber on the three grades of carbon black, respectively. Two separate inelastic neutron scattering instruments were used in these studies, the filter analyzer neutron spectrometer (FANS) and the Fermi chopper time-of-flight (ToF) spectrometer. These instruments cover different energy ranges and have different resolution capabilities, which allow us to examine a range of vibrational frequencies, especially very low frequency (long wavelength) motions not readily accessible by optical spectroscopy (IR and Raman). We find that while the FANS for all three types of samples show only subtle differences, more significant differences in the ToF spectra are observed. These differences are attributed to variations in interactions between the polymer with the carbon black surface and are correlated with the dynamic mechanical behavior of the filled polymers.

INELASTIC NEUTRON SCATTERING

Inelastic neutron scattering has been used for many years to examine vibrational motions and local dynamics in polymers.³ A number of different techniques fall into the category of inelastic neutron scattering including filter analyzer spectroscopy, time-of-flight spectroscopy, back-scattering spectroscopy, and neutron spin echo spectroscopy. In this study we will use the first two methods. While earlier studies were able to examine the influences of crosslinking, and the presence of fillers and additives on inter- and intrachain vibrational motions, they were limited in utility by poor signal to noise ratios due to low incident flux and by poor instrument resolution. More recent studies utilizing inelastic neutron techniques have been dominated by research groups in Europe and Asia. Among these studies are examinations of bulk polymers such as polybutadiene,^{4,5,6} polyethylene,^{7,8} polyisobutylene,^{9,10} polypropylene,¹¹ polyisoprene,¹² poly(vinyl acetate),¹³ and poly(*p*-phenylene vinylene),¹⁴ block copolymers,¹⁵ and carbon blacks.¹⁶ Most of these reports have focused on single component systems. We are aware of one study on the dynamics of poly(dimethyl siloxane) in the presence of fumed silica filler.¹⁷ With recent advances in instrumentation capabilities and neutron flux in the United States and at the National Institute of Standards and Technology (NIST) in particular, it is currently an optimum time to re-examine the use of inelastic neutron scattering techniques for probing vibrational motions in polymers.

The most common forms of spectroscopy which probe vibrational motions in polymers are infrared and Raman spectroscopy. However, polymers filled with carbon black and other fillers are ill-suited to the traditional optical spectroscopy methods since the samples are opaque. The opacity of the samples makes it extremely difficult to pass the probing radiation through the sample. Inelastic neutron methods are not restricted by the lack of penetration by the incident radiation into the sample. Parker et al.¹⁸ have performed a comparison of infrared, Raman, and inelastic neutron spectra obtained from various carbon black-filled polymers. Parker et al. found that infrared

spectroscopy was poorly suited to look at many filled polymers, and while they concluded that Raman spectroscopy was the method of choice for the quality of data, not all samples were suitable for Raman spectroscopy. Conversely, Parker et al. found that the inelastic neutron technique could be successfully applied to all samples, however, the method was limited to observations on the hydrogen containing parts of the samples. Both the Raman and inelastic neutron methods suffered from a lack of a suitable data base for spectral comparisons.

A detailed theoretical discussion of neutron scattering is beyond the scope of this paper. The interested reader is referred to the monograph by Higgins and Benoit.¹⁹ We will briefly summarize the basics of the neutron scattering technique for clarity. Any scattering technique involves the interaction of an incident beam of radiation with the sample. Typically, the interaction can be classified as either elastic (wavelength/energy conserved) or inelastic (wavelength/energy changed). The strength of scattering (scattering contrast) is due to the different interaction mechanisms between the incident radiation and the sample. In light scattering, the contrast is due to refractive index differences in the sample. In x-ray scattering, the contrast is due to electron density differences in the sample. In neutron scattering, the contrast is due to the different scattering lengths, b_i , of the different atomic nuclei in the sample, which also depend on the isotope and spin state of the i th nucleus. Under normal conditions, the spins are distributed randomly over the atoms (nuclear spin correlation can only occur at low temperatures, less than 1 mK). The average of the scattering lengths, \bar{b}_i , overall spin states of a particular nucleus is called the coherent scattering length, and the root mean square deviation of the distribution of b_i from \bar{b}_i defines the incoherent scattering length. The coherent cross section, σ_{coh} , and incoherent cross section, σ_{inc} , are related to the scattering lengths through Equation (1).

$$\sigma_{\text{coh}} = 4\pi(\bar{b}_i)^2 \quad (1a)$$

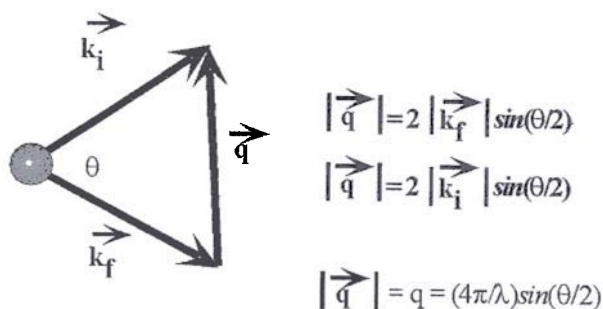
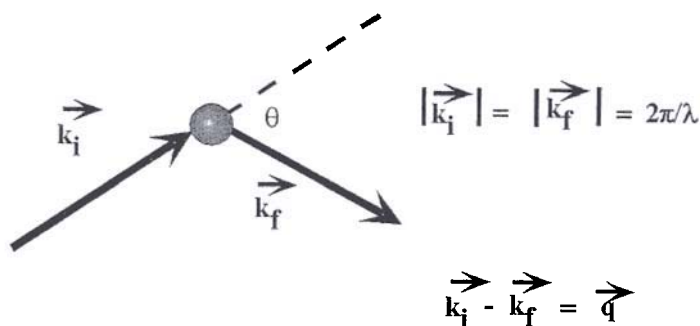
$$\sigma_{\text{inc}} = 4\pi[\overline{b_i^2} - (\bar{b}_i)^2] \quad (1b)$$

The values of the coherent and incoherent cross sections vary randomly across the periodic table, and also can differ substantially for different isotopes of the same element. The scattering contrast in a polymer sample is typically obtained through isotopic labeling with deuterium. The differences in the values of the coherent and incoherent scattering cross sections between hydrogen ($\sigma_{\text{coh}} = 1.759$ barn, $\sigma_{\text{inc}} = 79.90$ barn, $\bar{b} = -3.74$ fm) (1 barn = 1×10^{-28} m²) and deuterium ($\sigma_{\text{coh}} = 5.597$ barn, $\sigma_{\text{inc}} = 2.04$ barn, $\bar{b} = 6.674$ fm) are responsible for much of the success of small-angle neutron scattering methods. The negative value of the scattering length for hydrogen should be noted.

It can be shown that the coherent part of the scattering contains interference terms which provide all the structural information about the sample. The most familiar examples of neutron scattering are small-angle neutron scattering (SANS) experiments. In SANS experiments, the dominant part of the measured scattering intensity corresponds to elastic scattering with minor contributions from incoherent scattering of the sample. The scattering intensity is measured as a function of angle, θ , or momentum transfer, q ($= (4\pi/\lambda)[\sin(\theta/2)]$), Figure 1(a). After applying corrections to remove the incoherent scattering, the small angle neutron scattering signal provides the static structure factor, $S(q)$, containing structural information but no dynamic information.

The incoherent part of the scattering comes from the correlation of the spatial position of the nucleus at different times. Inelastic neutron scattering is therefore a powerful tool for the study of dynamic effects. Since inelastic scattering from polymers is usually dominated by the strong incoherent scattering from hydrogen, motions and vibrations of polymer chains can readily be measured. In inelastic neutron scattering experiments, the energy and scattering angle of the scattered neutrons are measured, therefore, the scattering as a function of energy or momentum is obtained, Figure 1(b). If we consider only one-phonon processes, i.e., the incident neutron can emit or absorb only one quantum of vibrational energy, then the incoherent cross section is directly

(a)



(b)

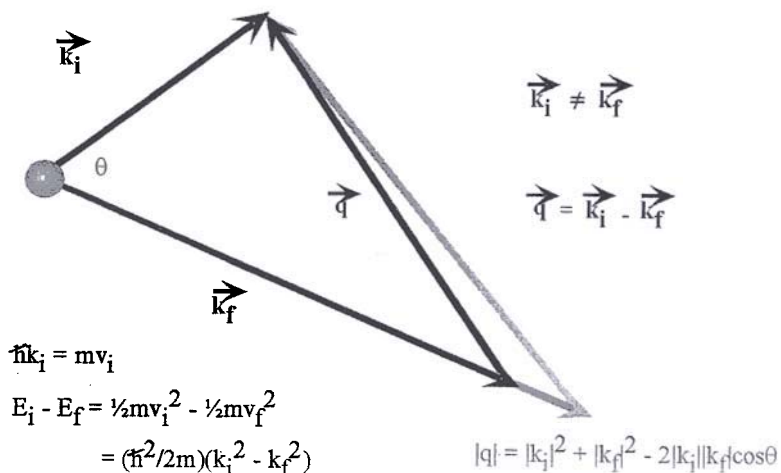


FIG. 1. — Schematic diagrams showing the relationships between the energies of the incident and scattered neutrons and the momentum transfer, q . (a) Elastic scattering case. (b) Inelastic scattering case.

proportional to the density of vibrational modes of the sample, $g(\omega)$ (fraction of modes with frequencies between ω and $\omega + d\omega$):

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE} \right)_{inc, \pm 1ph} &= \frac{k_f}{4\pi k_i} \sigma_{inc} S_{inc}(\vec{q}, \omega) \\ &= \frac{k_f}{4\pi k_i} \frac{3\sigma_{inc} \hbar \exp(-2W)}{2M} \frac{\langle |\vec{q} \cdot \vec{e}|^2 \rangle_\omega}{E} \left\langle n + \frac{1}{2} \pm \frac{1}{2} \right\rangle g(\omega) \end{aligned} \quad (1)$$

Here, $E = E_i - E_f = \hbar\omega$ is the energy transfer, M is the mass of the nucleus, $\exp(-2W)$ is the so-called Debye-Waller factor, and the expression $\langle |\vec{q} \cdot \vec{e}|^2 \rangle_\omega$ denotes an average of the product of the wavevector transfer, \vec{q} , and the phonon polarization vector, \vec{e} , overall vibrational

modes at the frequency, ω . The temperature dependent Bose population factor is given as $\langle n \rangle = 1/[\exp(E/kT) - 1]$.

One advantage of inelastic neutron scattering over a predominately elastic scattering technique such as small-angle neutron scattering (SANS) is that there is no special need for isotopically labeled samples. Since the inelastic neutron scattering is dominated by contributions from hydrogen atoms, deuterium labeled samples, such as those necessary for SANS are not required. However, by selectively labeling certain sites, dynamic information on the unlabeled portions of the sample can be elucidated. An example of the use of such selective labeling is demonstrated in the interpretation of our data below. The second advantage of inelastic neutron scattering is that optical selection rules which restrict the vibrational transitions that can be observed by infrared or Raman spectroscopy do not apply to the inelastic neutron scattering method. Therefore, additional information can be obtained on the various vibrational states.

EXPERIMENTAL

MATERIALS

The materials used in this study were supplied by Sid Richardson Carbon Company.²⁰ The polymer used was a synthetic polyisoprene (Natsyn® 2200, Goodyear Tire & Rubber Co.).²⁰ The physical characteristics of the polymer were given by the manufacturer as follows: microstructure content = 98% cis, the weight-average molecular mass, M_w , between 755,000 and 955,000 g/mol, and the number-average molecular mass, M_n , between 240,000 and 350,000 g/mol. We assume a literature value for the glass-transition temperature (T_g) of -72°C .²¹

The carbon blacks used in this study consisted of three different grades specified as N299, G299, and N762. The G299 carbon black is the graphitized version of the N299 carbon black and was prepared by heating a sample of N299 carbon black under nitrogen atmosphere in an induction furnace at 2700°C . The carbon blacks were characterized using nitrogen adsorption according to Brunauer, Emmett and Teller²² (BET) (ASTM D 4820) to obtain the surface area, dibutyl phthalate (DBP) absorption (ASTM D 2414) to obtain the void volume in the carbon black aggregates, and by compressed DBP (CDBP) absorption (ASTM D 3493), which is similar to the DBP absorption but the carbon black has been compressed to reduce the interaggregate voids. The results of the three tests on the carbon blacks are given in Table I.

The carbon blacks were compounded into the polymer without any other additives. Compounding was performed in a Haake Rheocord System 90 equipped with a Model 600 internal mixer.²⁰ A starting temperature of 50°C , rotor speed of 90 revolutions per minute (rpm), and a compounding time of 5 min were the conditions used to prepare each sample. Three concentrations of carbon black-filled samples were prepared: 20 parts (by mass) of carbon black per 100 parts of rubber (20 phr) (phr is defined as parts by mass of the component per one hundred parts by mass of the rubber) (nominal mass fraction of carbon black = 16.7%), 30 phr (nominal mass fraction of carbon black =

TABLE I
PHYSICAL CHARACTERISTICS OF THE CARBON BLACKS

Carbon black ID	N ₂ BET surface area, m ² /g	DBP, cm ³ /100 g	CDBP, cm ³ /100 g
N299	102.4 ± 0.7 ^a	123.7 ± 0.6	106.1 ± 0.8
G299	92.5 ± 0.4	120.2 ± 0.6	103.4 ± 0.8
N762	27.3 ± 0.2	63.9 ± 0.4	60.5 ± 0.6

^a The \pm values in the table represent one standard deviation.

23.1%) and 50 phr (nominal mass fraction of carbon black = 33.3%). We will refer to the samples by their initial carbon black concentration in phr.

The samples were also characterized mechanically on a Rheometrics SR5000 controlled stress rheometer. The mechanical characterization is for relative comparison only and measurements were conducted on the pure polymer and polymer filled with 30 phr of each of the three different carbon blacks. No mechanical measurements were performed on the extracted samples since preparation of void free samples was not possible. Sufficient amounts of each sample were placed between 25 mm parallel plate fixtures heated to 100 °C. The sample gap for all samples was 2.0 mm and a dynamic frequency sweep was performed between 0.1 and 100 rad/s at fixed strain of 1%.

SOXHLET EXTRACTION

The carbon black-filled samples containing only bound rubber were prepared by Soxhlet extraction of the compounded samples described above. Approximately 2 to 3 g of the carbon black-filled polymer, cut into pieces of nominal size, 2 mm × 2 mm × 2 mm, were placed in a Soxhlet extraction thimble (Whatman, single thickness, cellulose extraction thimbles, 33 mm diameter, 80 mm long).²⁰ Each Soxhlet apparatus was equipped with a 500 mL round-bottom flask filled with 300 mL of toluene. The apparatus was heated to a gentle reflux and the extraction was conducted for 72 h. After 72 h, the thimbles were removed from the Soxhlet apparatus and rinsed with warm, fresh toluene. The residue was then scraped out of the thimbles and solvent allowed to evaporate. The extracted carbon black samples were then placed in a vacuum oven at 100 °C for 24 h to remove the last traces of toluene. During the extraction, some of the carbon black goes through the extraction thimbles. The amount of carbon black lost during the extraction was determined by collecting the solution in the round-bottom flask and removing the solvent by evaporation, leaving the soluble polymer fraction and carbon black. The amount of carbon black lost during the extraction was determined to be less than 1% of the original amount of carbon black. The amount of carbon black in the extracted samples that was lost during the extraction process was determined by thermogravimetric analysis (TGA).

THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermogravimetric analysis (TGA) was performed on a Perkin Elmer 7 Series Thermal Analysis System equipped with a nitrogen purge. Each sample, weighing 0.005 to 0.010 g, was placed into the sample pan and heated under nitrogen purge from 30 to 900 °C at a heating rate of 40 °C/min. TGA on the unextracted samples was also performed to verify the initial compositions of the samples. A summary of the TGA results is given in Table II. With the exception of the G299 filled sample, the amount of bound polymer decreases as the initial concentration of carbon black increases. This is consistent with prior reports on the variation of bound rubber content as a function of the initial carbon black concentration.¹ The TGA results on the extracted N762 filled polymer indicate an extraordinarily high amount of bound rubber. Prior studies indicate that bound rubber content decreases with decreasing surface area. It was noted during the extraction process that the N762 filled samples tended to clog the Soxhlet extraction thimbles, which may explain the anomalous bound polymer data.

INELASTIC NEUTRON SCATTERING

Two complementary inelastic neutron scattering instruments were used for these measurements, the filter analyzer neutron spectrometer (FANS) and the Fermi chopper time-of-flight spectrometer (ToF). Both instruments are located at the NIST Center for Neutron Research (NCNR). For both sets of experiments, approximately 2 g of sample are pressed into a film, roughly 2 cm × 2 cm. The film is placed between aluminum sheets which are held together in a mounting bracket to form a

TABLE II
THERMOGRAVIMETRIC ANALYSIS OF CARBON BLACK-FILLED SAMPLES

Carbon black	Condition	20 phr	30 phr	50 phr
N299	As received	17.1 ^a	23.4	33.3
	Extracted	41.9 (58.1)	45.5 (54.5)	71.7 (28.3)
G299	As received	16.8	23.1	33.4
	Extracted	76.3 (23.7)	60.9 (39.1)	84.4 (15.6)
N762	As received	16.9	22.6	33.0
	Extracted	18.9 (81.1)	27.8 (72.2)	—

^a All values represent mass fractions in percent of carbon black. Values in parentheses give the mass fractions in percent of bound rubber. Based on previous measurement data, the estimated relative standard uncertainty on the values in the table above is $\pm 1.0\%$.

sandwich-type sample geometry. The samples are then mounted in a cryostat which is sealed under vacuum.

The experiments using the filter analyzer spectrometer (FANS) were performed at 10 K. A schematic of the instrument is shown in Figure 2. In this experiment, monochromatic neutrons (two monochromator selections, copper (Cu) or pyrolytic graphite (PG)) of variable energy, E_i , are inelastically scattered by the sample through an angle of 90° and detected at fixed final energy, E_f , through a low-pass Bragg cutoff filter. The cutoff conditions are determined by the cutoff filter material. When beryllium is used as the cutoff filter, the cutoff energy is ≈ 3 meV and when the beryllium filter is used in series with a powdered graphite filter, the cutoff energy is ≈ 1.1 meV. These two conditions result in substantially different energy resolutions. Experiments were performed using both types of cutoff filters.

The time-of flight spectrometer experiments were performed at 193 K. A schematic of the ToF instrument is shown in Figure 3. In this instrument a monochromatic beam is produced by monochromator crystals. A Fermi chopper is used to produce neutron bursts at well defined times. The scattered neutrons are detected in an array of 60 detectors as a function of time after the neutron burst produced by the Fermi chopper. The scattering function, $S(q, \omega)$ is integrated overall q to give, $S(\omega)$. An incident wavelength of 4.8 \AA and instrument time channel width of $6 \mu\text{s}$ was used, giving an energy resolution of 0.15 meV near zero energy transfer.

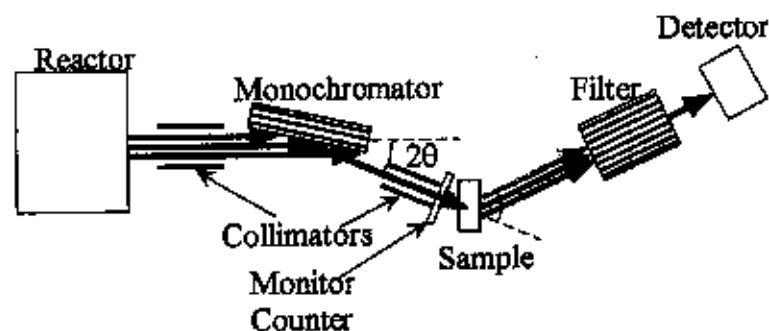


FIG. 2. — Instrument schematic of the filter analyzer neutron spectrometer.

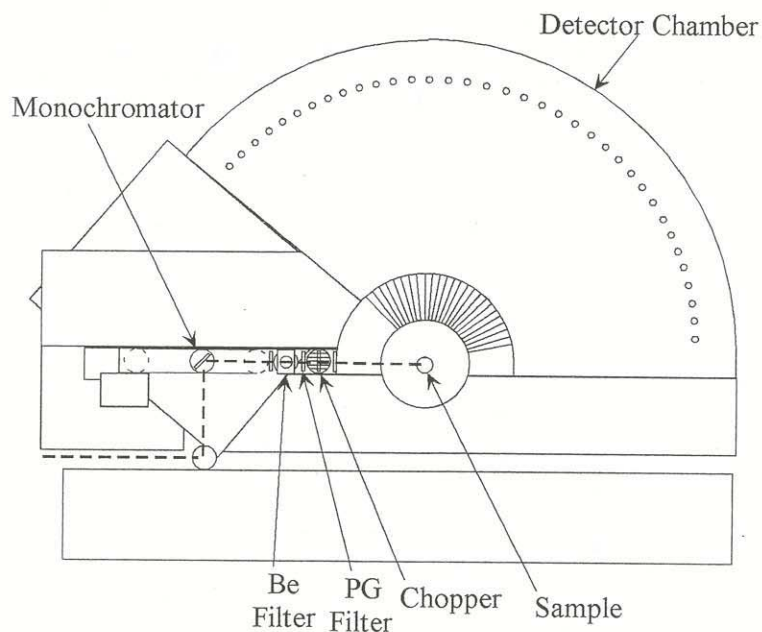


FIG. 3. — Instrument schematic of the Fermi chopper time-of-flight spectrometer.

RESULTS

DYNAMIC MECHANICAL BEHAVIOR

The results comparing the dynamic storage modulus, G' , and dynamic loss modulus, G'' , for each sample and the dynamic viscosity, η^* , and $\tan \delta (= G''/G')$ against the unfilled polymer are shown in Figure 4. Distinct differences in the dynamic behavior of the samples were observed for each of the three different carbon blacks at the same loading levels. All of the carbon blacks increased the moduli values above those of the pure polymer. The G299 carbon black produced the greatest enhancement in the moduli and the N762 carbon black gave the lowest degree of enhancement. Similar behavior was observed for the dynamic viscosity where the G299 black-filled sample had the highest viscosity and the N762 filled sample had the lowest viscosity. We also noted that the N762 filled sample had the highest crossover frequency between G' and G'' and the other two samples had crossover frequencies less than the lowest frequency which was measured. This supports our hypothesis that the polymer dynamics vary for each of the different carbon black-filled samples and that we can potentially observe these differences in the inelastic neutron scattering spectra.

FILTER ANALYZER NEUTRON SPECTROSCOPY

The raw filter analyzer data were reduced by subtracting the measured scattering of the empty aluminum packet to obtain a background corrected spectrum. We assume the contributions to the inelastic scattering by the carbon black are negligible because of the small value of the total scattering cross-section for carbon. We have also verified that the scattering intensity measured by both techniques for carbon samples with very little hydrogen are orders of magnitude smaller than in our experiments. Since the carbon black-filled polyisoprene samples all have slightly different masses and different C/H ratios, for ease of comparison of the features, the background corrected intensities were normalized so that the area under each spectrum is unity. This is accomplished by dividing the number of detector counts at each energy by the integrated neutron counts over the

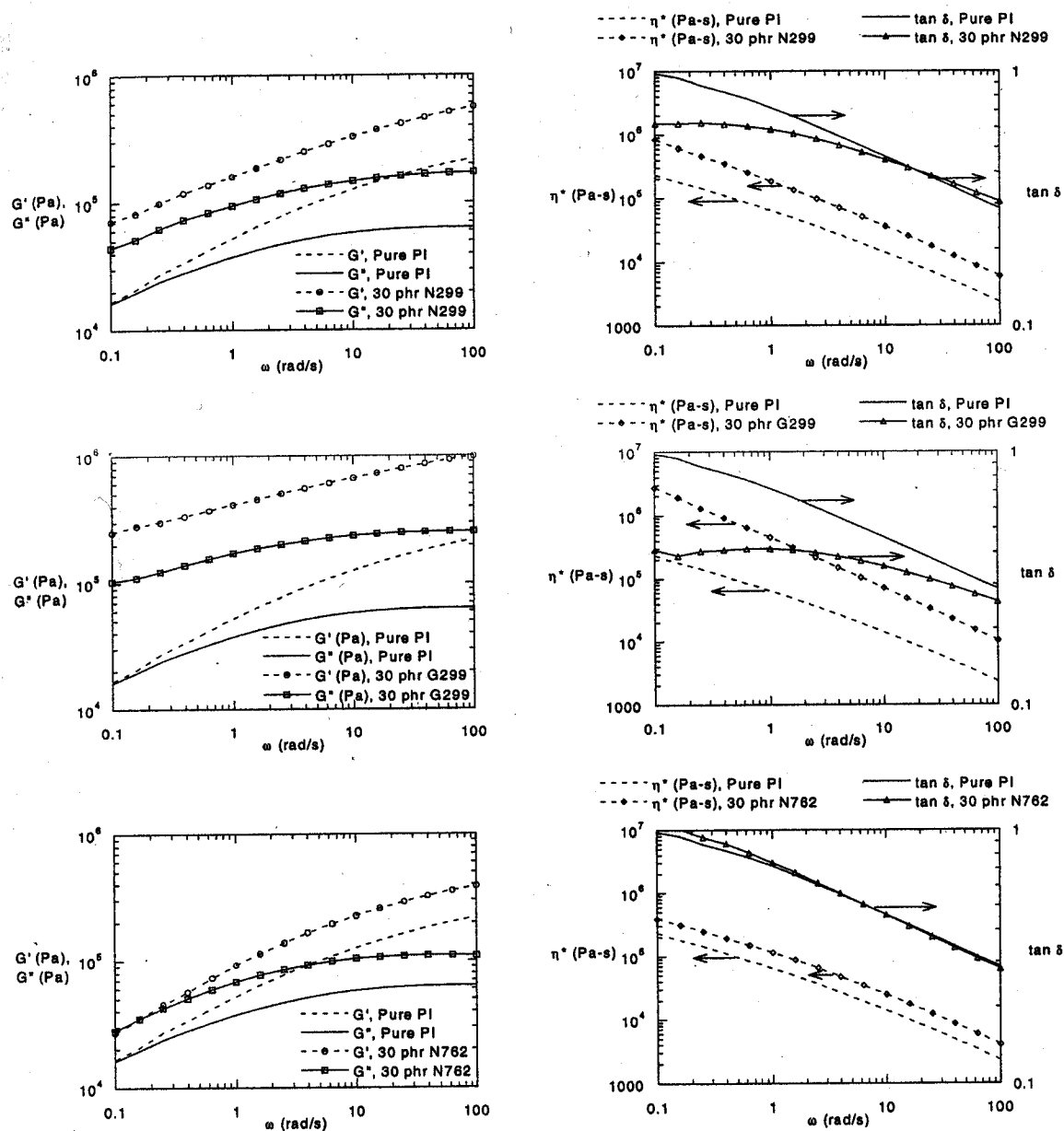


FIG. 4. — Comparison of the dynamic mechanical behavior of different carbon blacks (concentration of carbon blacks fixed at 30 phr) in polyisoprene taken at 100°C at a fixed strain of 1%. Top row—N299 carbon black; middle row—G299 carbon black; bottom row—N762 carbon black. Left hand column compares G' and G'' of the filled material against the pure polymer. Right hand column compares η^* and $\tan \delta$ of the filled material against the pure polymer. Based on prior measurements on this equipment, the standard relative uncertainties for each data point are smaller than the plotting symbols.

entire energy range of the experiment. Data reduced in this fashion will be referred to as the area normalized spectra.

The Cu monochromator FANS results for the pure polyisoprene are compared with the extracted samples in Figure 5. All the extracted samples used to obtain Figure 5 had an initial carbon black concentration of 30 phr. The Cu monochromator allows the FANS to cover a broad energy range (35 to 200 meV) with moderate energy resolution (1 meV resolution at low energies and 3 meV resolution at high energies). There do not appear to be any significant shifts in the peak energies nor in the relative intensities of the features in the spectra.

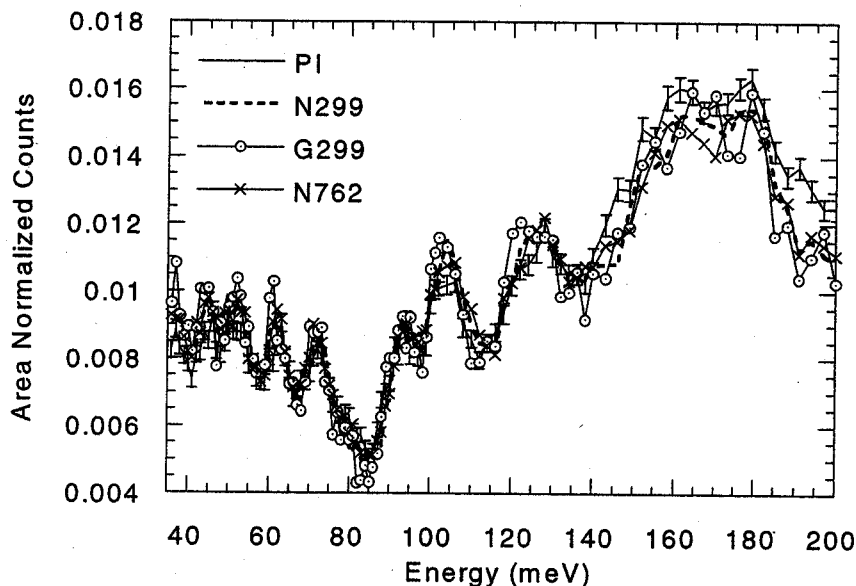


FIG. 5. — Filter analyzer spectrometer data taken with the copper monochromator showing the incoherent scattered neutron intensity as a function of energy for the pure polyisoprene and the three carbon black-filled polyisoprene samples. Bars on the data points for the inelastic neutron data indicate typical standard uncertainties for each point based on the detector sensitivity and counting statistics.

The PG monochromator FANS results for the pure polyisoprene and the extracted samples are shown in Figure 6. As in Figure 5, the initial carbon black concentration was 30 phr. With the PG monochromator, the FANS covers a much narrower and lower range of energies (14 to 40 meV). The energy resolution is approximately 0.5 meV. The PG monochromator data show some subtle systematic differences as a function of the carbon black type which correlate with

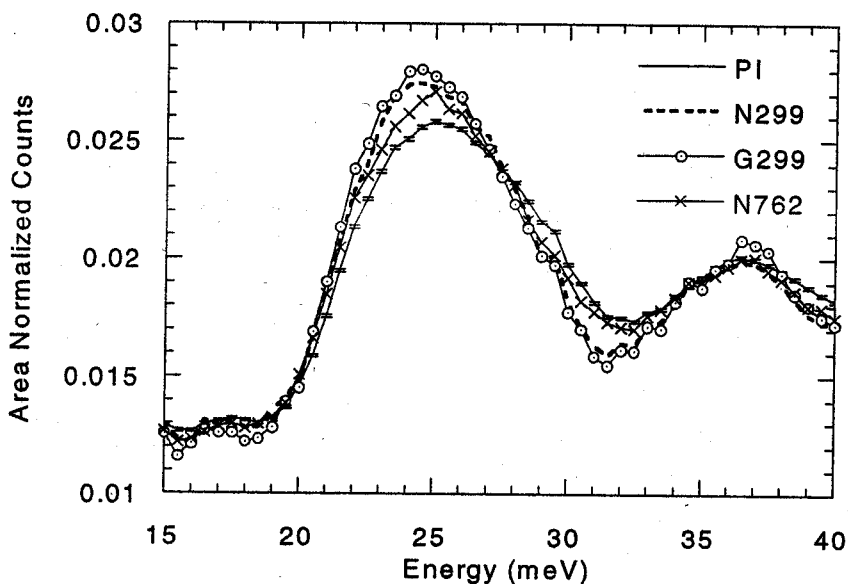


FIG. 6. — Filter analyzer spectrometer data taken with the polycrystalline graphite monochromator showing the incoherent scattered neutron intensity as a function of energy for the pure polyisoprene and the three carbon black-filled polyisoprene samples. Bars on the data points are shown only for the pure polyisoprene data for clarity and indicate typical standard uncertainties for each point based on the detector sensitivity and counting statistics and are representative of the uncertainties for the other samples.

the trends observed in the mechanical behavior. The main features in Figure 6 are two maxima at approximately 36.5 meV and 25 meV. The peak at 36.5 meV shows little variation between the four samples. Conversely, the peak at 25 meV shifts to slightly lower energies in the presence of carbon black. The G299 carbon produces the biggest shift, followed by the N299 carbon black, and the N762 carbon black produces the smallest shift in the peak position. The small shift produced by the N762 containing sample may be due to the fact that all the unbound polymer was not removed from the sample. However, this same relative ordering of the carbon blacks was observed for the enhancement of the modulus and viscosity values. Also the minimum between the two peaks shifts in a fashion similar to the maximum at 25 meV, and the ratio of intensities between the peak maximum at 25 meV and the minimum around 32 meV increases as the reinforcement effect of the carbon blacks increases.

The motions probed in the energy range covered with the Cu monochromator correspond to localized vibrational and torsional motions in the isoprene monomer unit. These motions have been identified previously by infrared (IR) and Raman spectroscopy methods. An infrared spectrum of pure polyisoprene is shown in Figure 7 for comparison ($1 \text{ meV} = 8.07 \text{ cm}^{-1}$). The peak positions of the IR spectra are in reasonable agreement with the FANS spectra. The insensitivity of the Cu monochromator FANS spectra to the type of carbon black indicates that despite being bound to the surface of the carbon black, the localized vibrational modes in the monomer units of the bound polymer are unaffected at this experimental temperature.

The energy range probed using the PG monochromator is associated with longer length scale motions such as rotations and torsions of the polymer backbone and cooperative motions between monomer units. These modes are more strongly affected by inter- and intra-chain interactions (or by interactions with filler particles) than the localized vibrations occurring at higher frequencies. Interpretation of these results follows the next section.

FERMI-CHOPPER TIME-OF-FLIGHT SPECTROSCOPY

The ToF results for the pure polyisoprene are compared with the extracted samples in Figure 8. As with the FANS data, the extracted samples used to obtain Figure 8 had initial carbon black concentrations of 30 phr. We note that in the FANS technique, incident neutrons emit (create) phonons

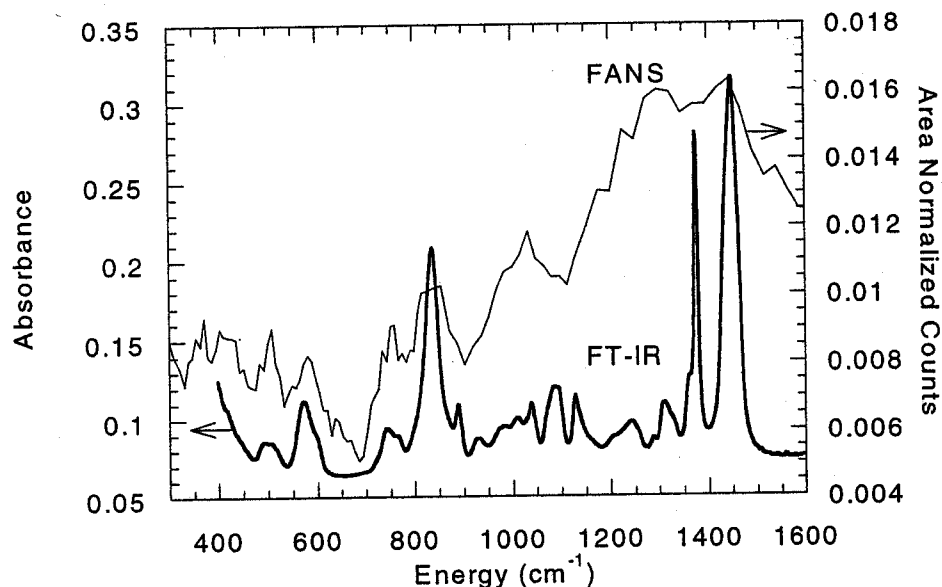


FIG. 7. — Comparison of the Fourier transform infrared (FT-IR) spectrum and FANS spectrum of the pure polyisoprene ($1 \text{ meV} = 0.124 \text{ cm}^{-1}$).

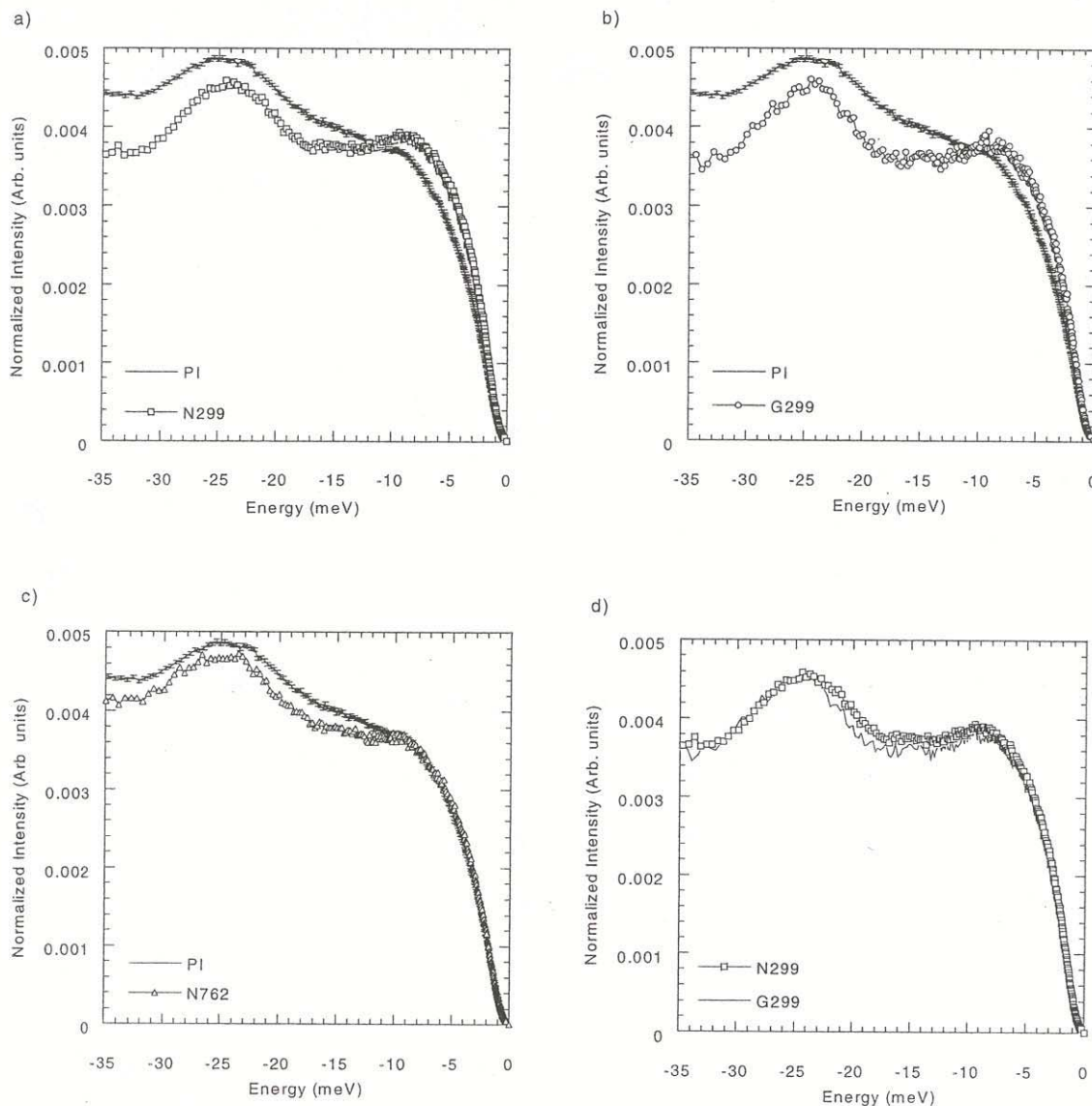


FIG. 8. — Data taken from the Fermi chopper time-of-flight spectrometer showing the density of states, $g(\epsilon)$, for the pure polyisoprene and (a) 30 phr N299 filled polyisoprene; (b) 30 phr G299 filled polyisoprene; (c) 30 phr N762 filled polyisoprene. (d) Comparison of N299 and G299 filled samples. Bars on the data points are shown only for the pure polyisoprene data for clarity and indicate typical standard uncertainties for each point based on the detector sensitivity and counting statistics and are representative of the uncertainties for the other samples.

in the sample, whereas the ToF technique measures neutrons which have absorbed thermally excited phonons in the sample. Hence, the scale for energy transfer, $\Delta E = E_i - E_f$, is positive for FANS spectra and negative for the ToF data. The ToF instrument is also more sensitive to lower energy modes than the FANS. The data in Figure 8 are presented in a density of states formalism. The ToF technique measures $S(q, \omega)$, therefore, by integrating overall q at each ω , the so-called density of vibrational states, $g(\epsilon)$, is obtained. The data in Figure 8 have also been normalized over the entire energy range of the instrument so the area under the curve is unity.

For clarity, each of the density of states spectra for the filled polyisoprenes is compared separately with the density of states for the pure polyisoprene. The primary features in the density of states spectra are a maximum at about -25 meV and another maximum (or shoulder) at about -9 meV.

The pure polyisoprene has the broadest maximum at -25 meV and no maximum at -9 meV. The samples filled with the N299, Figure 8(a), and G299, Figure 8(b), carbon blacks develop a pronounced peak at -9 meV and the peak at -25 meV shifts to -24 meV and narrows for both carbon blacks. In contrast, the N762 filled sample develops only a weak shoulder at -9 meV, and the peak at -25 meV narrows slightly compared to the pure polyisoprene, Figure 8(c). Again, we note that the N762 containing sample may contain a significant fraction of unbound polymer due to incomplete extraction. A direct comparison of the density of states between the N299 and G299 carbon blacks is shown in Figure 8(d). The peak breadth at -24 meV is slightly narrower for the G299 filled sample.

These results are consistent with the shifts of the 25 meV peak in the FANS spectra discussed previously. The shifts are more well-defined in the FANS spectra than the ToF data due to the lower sample temperature and slightly better energy resolution of the FANS instrument in this energy range. The same relative trend which was observed in the enhancement of dynamic mechanical properties and the FANS features among the carbon blacks was also observed in the ToF data. The extent of narrowing of the peak at -24 meV in the ToF spectra also correlates with the relative reinforcement by each type of carbon black.

In Figure 9, we show some preliminary data examining the effect of the initial carbon black concentration on the ToF spectra for the bound polymers. A comparison is shown between an extracted 30 phr N299 sample and an extracted 50 phr N299 sample. The extracted 50 phr sample contains less bound polymer (mass fraction of 28.3%) than the extracted 30 phr sample (mass fraction of 54.5%). The peak at -24 meV is slightly narrower and the peak at -9 meV is slightly higher in intensity for the 50 phr extract compared with the 30 phr extract. Further work is in progress to confirm the concentration dependence observed here.

DISCUSSION

The trends in the inelastic neutron scattering data are systematic and well-defined, and we now present a physical interpretation of the data. The FANS and ToF experiments are done at sub- T_g temperatures to eliminate broadening of the spectral features due to large amplitude thermal motions. We believe the sub- T_g dynamics behavior reported in this and other studies cited below are relevant to applications where filled polymers above T_g undergo high frequency deformations which are faster than the polymer librational frequencies. The lack of sensitivity to the type of carbon black in the Cu monochromator FANS data indicates that no specific interactions between chemical bonds are involved in the binding of the polymer, therefore, the strength of the polymer-filler interactions for each of the three types of carbon blacks is the same and only the number of interactions varies.

Interpretation of the PG monochromator FANS and ToF data is based upon prior work by Frick and Fetters,¹² who have examined dynamics of glassy polyisoprene by ToF neutron techniques. Frick and Fetters used selectively labeled polyisoprenes to distinguish between the methyl group dynamics and the main chain backbone dynamics. To examine the methyl group dynamics, all backbone hydrogen atoms were substituted with deuterium atoms, while the main chain backbone dynamics were studied in a sample with deuterated methyl groups. By examining these two samples, they concluded that a peak at 23.5 meV in the vibrational density of states spectrum corresponded to the librational motion of the methyl groups, while a peak at 7 meV corresponded to various librational modes of the polymer backbone. These two peaks correspond directly with the peaks we observe at 25 to 24 meV and 9 to 8 meV, respectively. Frick and Fetters also state that the energy of the methyl group librational mode is related to the energy difference between the librational ground state and the height of the potential well in which the methyl group protons move. In a sterically hindered polyisobutylene, the methyl group librational mode was observed at 40 meV.²³

From the work of Frick and Fetters, we can infer the following on the dynamics of polyisoprene in the presence of various carbon blacks. We remind the reader that the ToF results were obtained at 193 K, which is approximately 8 K below the reported T_g for polyisoprene. Over the range of vibrational energies covered by our experiments, the polyisoprene bound to the G299 carbon black shows the highest degree of backbone librational motion from the ToF data and the methyl groups in this sample have the lowest energy difference between the librational ground state and the potential well maximum from the PG monochromator FANS data. The lowest energy difference between the ground state and the potential well maximum implies that the methyl group librations are most easily accomplished in the G299 filled sample. This is in contrast to the polyisoprene in the N762 carbon black-filled samples, which show very little backbone librational motion and a higher energy barrier to methyl group librations. The conclusions about the N762 containing sample may be complicated by the incomplete removal of the unbound polymer. Since the ToF experiments are done below the T_g of the polyisoprene, one would expect a lack of backbone motion in the pure polymer. However, the bound polymer in the G299 filled sample has a higher degree of mobility than the pure polymer at the same temperature, since the backbone motions are more evident and the energy barrier to methyl group motions is lower. The polymer bound to the N299 carbon black also has a higher degree of mobility compared to the pure polyisoprene.

Our interpretation of the mobility of the bound polymer does not appear to be consistent with the prevailing opinion of bound polymer dynamics.¹ Most studies of bound polymer have concluded that the polymer motion in bound rubber is more restricted than in the unfilled polymer. In an attempt to reconcile our current results with prior data, we have considered the presence of residual solvent as a possible reason for producing increased mobility in our experiments. Thermogravimetric analysis

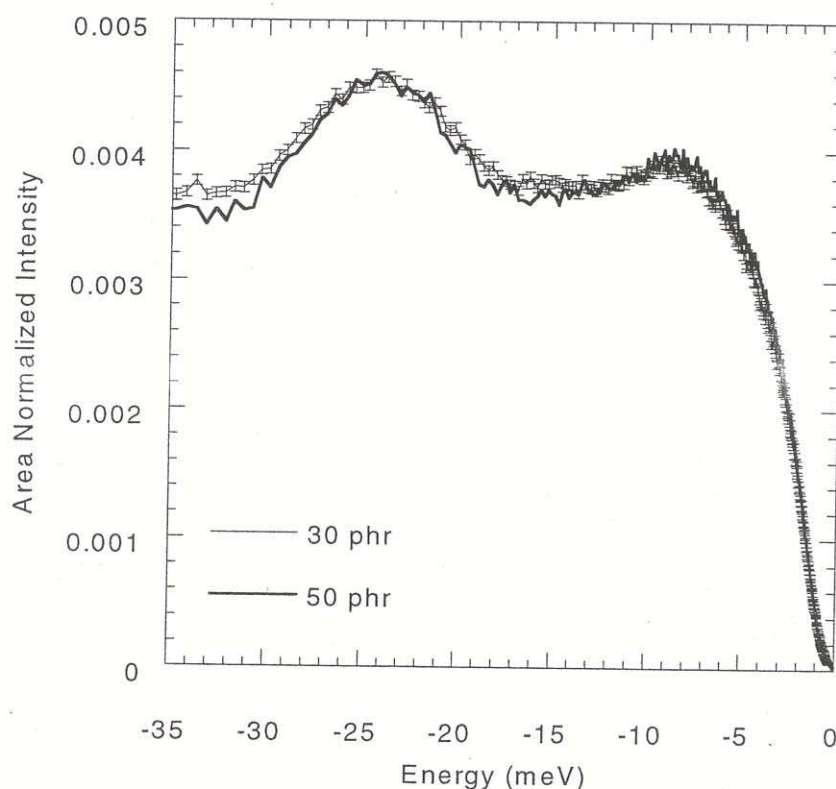


FIG. 9. — $g(\epsilon)$ for 30 phr and 50 phr N299 extracted samples. Bars on the data points are shown only for the 30 phr data for clarity and indicate typical standard uncertainties for each point based on the detector sensitivity and counting statistics and are representative of the uncertainties for the other sample.

traces on the extracted samples show no mass loss on heating until approximately 400 °C. This is well above the boiling point of toluene (= 110.6 °C), which is used for the extraction, therefore, the apparent increase in mobility cannot be due to the presence of residual solvent.

The prior studies on bound polymer have been conducted using a wide variety of experimental techniques such as dilatometry,²⁴ dynamic mechanical behavior,²⁵ and NMR measurements.^{26,27,28,29,30,31} Attempts to quantify differences in T_g in the presence and absence of filler have been inconclusive.²⁴ The NMR data examining dynamics in filled polymers are the most numerous, yet certain inconsistencies are present in the data. Except for one study,²⁶ all the cited NMR results support the existence of a more rigid layer of polymer surrounding the filler particles. It is important to note these results are for temperatures above the glass-transition temperature. Very small shifts in the T_g of the filled polymers are reported by NMR (< 4 °C). These small T_g shifts do not appear to be consistent with the dramatic increase in rigidity of the bound polymer layer. Nearly all the NMR data below the glass-transition temperature indicate much more restricted mobility than above T_g , with no differences in the filled and unfilled polymer mobility below T_g . In contrast, a recent study by Litvinov and Steeman³¹ indicated that the spin-spin relaxation time, T_2 for an extracted, carbon black-filled polymer was longer than the T_2 of the same unfilled polymer at temperatures below the glass-transition temperature. This would indicate that the mobility of the filled, bound polymer is greater than the mobility of the unfilled polymer at low temperatures. Also, the temperature dependence of T_2 indicated that while the value of the glass-transition temperature differed slightly between the filled and unfilled polymers, the breadth of the transition was much greater for the filled polymer. Hence for temperatures slightly above T_g , the polymer dynamics of the bound, filled polymer are slower than the unfilled polymer, but at much higher temperatures, the T_2 values are similar, therefore the dynamics of the polymer in both cases are similar. A similar convergence of T_2 values below T_g was not observed by Litvinov and Steeman, therefore the mobility of the bound polymer is always higher than the mobility of the unfilled polymer below T_g . Other NMR studies have found only a single T_2 value for temperatures below T_g . The results of Litvinov and Steeman appear to be consistent with the data presented here, which are obtained at sub- T_g temperatures.

A dilatometric study by Kraus and Gruver²⁴ also appears to support our conclusions. Kraus and Gruver found that the coefficient of thermal expansion of a carbon black-filled polymer is unchanged above T_g , but below T_g , the thermal expansion coefficient of the filled polymer is less than the value for the unfilled polymer. From this data, Kraus and Gruver conclude that the free volume of the filled polymer actually increases as the temperature is lowered below T_g . Since the free volume below T_g is greater in the filled polymer than in the unfilled polymer, one might conclude that the degree of mobility in the filled polymer below T_g must also be higher than in the unfilled case.

Estimates of the thickness of the bound polymer layer range from 2 nm²⁵ to 50 nm.³² Since the glass transition has been related to changes in local dynamics of molecules, studies of the glass-transition behavior in thin films³³ and confined media^{34,35} may be relevant to the discussion of the results presented here. Depending on the polymer-surface interaction, the measured T_g of a variety of polymers has usually been reported to decrease, however, instances of increases in T_g have also been reported. A source of this confusion is the variety of measurement techniques, polymer types and surface treatments used in these studies. The dynamic behavior of polymers near a surface in the vicinity of the glass-transition temperature is clearly not well understood, and we believe that the ideas of polymer dynamics in the presence of filler particles and the relationship to bound polymer and mechanisms of reinforcement may be related to these thin film studies in a fundamental manner.

CONCLUSIONS

We have observed qualitative differences in FANS and ToF spectra between pure polyisoprene and polyisoprene bound to carbon black. The observed changes in the inelastic neutron spectra appear to be correlated with the type of carbon black and the extent of reinforcement each carbon black produces when compounded with the pure polymer. We feel this study demonstrates the need to re-examine the dynamics of polymers in the presence of fillers more closely and exhibits the potential utility of inelastic neutron scattering studies to address issues related to the mechanisms of reinforcement in filled polymers. Future studies involve an examination of the temperature dependence of the spectral features using neutron back-scattering spectroscopy. Since these experiments do not rely on isotopically labeled samples, similar studies based on other fillers and polymers are also planned.

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